



**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application No.: 09/927,175  
Filing Date: August 10, 2001  
Applicant: Robert A. DiChiara Jr.  
Group Art Unit: 1762  
Examiner: Michael Barr  
Title: SURFACE PROTECTION OF POROUS CERAMIC BODIES  
Attorney Docket: 7784-000171

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Director of The United States Patent and Trademark Office  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

**DECLARATION OF ROBERT A. DICHIAARA, JR. UNDER 37 C.F.R. § 1.132**

1. I am the inventor of the current application. I am also the inventor of U.S. Patents 5,928,775 and 5,702,761, which are being discussed in the Office Action as the DiChiara reference.

2. I am a Technical Fellow with the Boeing Company and have been employed with Boeing since 1996 and prior to that with McDonnell Douglas since 1989. Previous positions include the Gillette Advanced Technology Lab, The Dow Chemical Company, and the Cabot Technical Center for Electronic Packaging. I have a Bachelors Science Degree in Ceramic Engineering from Alfred University and a Master of Science in Ceramic Engineering from the University of Illinois. All told I have worked in ceramics for 24 years, beginning with development of CaO stabilized ZrO<sub>2</sub> infrared windows and continuing through to my current technical position at Boeing. I have published 25 articles and written many others that could not be published due to their classified nature. I hold 13 U.S. patents and have about 17 patents

pending, including the current one. In my current position at Boeing I am a Ceramic Technical Fellow and Team Leader for development in many high technology programs for Boeing. I interface and have extensive contacts with NASA, the Air Force, and other major Boeing customers.

3. I have been asked to comment on emissivity agents and how they apply to my current invention. I understand the Examiner has taken the position that my prior patents suggest the use of emissivity agents in slurries containing silica and cordierite. I also understand the Examiner is citing other documents for the proposition that certain boron compounds are known emissivity agents for use in high temperature ceramics. The Examiner is correct on both counts. But it is my opinion that, despite the references being cited in prosecution of my application, my invention would not have been obvious to a person of skill in the art. Specifically, a person of skill in the art would not have expected boron compounds, even if some have been known to be emissivity agents in ceramic applications, to improve the temperature stability of tiles treated by slurries containing them in addition to the silica and cordierite of my earlier inventions.

4. Emissivity agents by definition increase the amount for rate of re-radiation of absorbed heat energy. In general, the temperature of a body depends on and is determined by the relative rates of heat absorption, re-radiation, and reflection. All things being equal, a body having emissivity agents will have a relatively higher rate of re-radiation. As a result, the equilibrium temperature of such a body will tend to be lower than it would be without the emissivity agent. In other words, emissivity agents can be added to ceramics to lower the temperature of a tile in a certain application. The action of an emissivity agent is physical in nature. It helps with the re-radiation of absorbed heat energy.

5. But the physical effect has nothing in principle to do with the ability of the chemical composition of the ceramic body to withstand a certain temperature. The presence of emissivity agents in the body may cause there to be more heat required to raise the tile to a certain temperature. But once the higher temperature is reached, the tile will loose strength. A person of skill in the art has no reason to believe that an emissivity agent, which as described above gives a physical effect only, would necessarily affect a chemical property such as high temperature stability.

6. On the basis of the above, I would say that the teachings of the references cited in the Office Action would not make my invention obvious to a person of skill in the art. As discussed, emissivity agents have a role to play, but is unrelated to any chemical effect of an increasing temperature stability of the coating and the tile.

7. I am also requested to comment on the breadth of the invention, i.e. whether a wide variety of boron compounds would be effective for use in my invention, or whether the effect should be limited to only the boron compound exemplified in my application (boron carbide).

8. In my career, I am very familiar with the development of high temperature tiles, such as for the space shuttle. The original tiles on the shuttle were made of silica fibers (called LI-900 or LI-2200). NASA made an first advancement on these tiles called FRIC (fiber reinforced ceramic insulation) in which they added aluminoborosilicate fiber (Nextel 312 fibers) to the silica fiber. This produced a stronger binding tile. Later NASA developed AETB (for aluminum enhanced thermal barrier), a tile that added alumina to raise the melting point or refractoriness of the tile. Lockheed then developed HTP tile that substituted boron nitride or boron carbide powder for the aluminoborosilicate fiber in AETB, producing similar tile results. The above developments indicate that boron and boron-containing materials have been used in high temperature ceramic tile to increase the tile mechanical strength.

9. Silica ( $\text{SiO}_2$ ) has a tendency to devitrify or crystallize above 2000°F, causing it to become weaker. Often, boron is added as a network modifier to silica, causing silica to have a lower melting point, and keeping the silica from devitrifying (crystallizing).

10. In my previous work, for example in U.S. 5,928,775 and 5,702,761, I invented coatings for a tile that used silica sol together with fine cordierite powders. The silica sol helped to bond the fine low expansion cordierite powders that get lodged into the top surface of the tile, producing a very durable tile surface. High emissivity agents such as SiC were sometimes added to the mix to raise the coating surface emissivity. I developed the prior art materials, not for space applications, but more for aircraft applications where a quick repairable coating was desired and it did not need to be fired. Further, it was to have the ability to produce a wear resistant surface where temperatures of exposure were approximately 2000°F.

11. For higher temperature conditions such as with space applications, I developed the current slurries and methods that use boron compounds. It was found that high temperature exposures of the tiles treated with the prior art slurries caused the coating to react with the tile and lower the tensile properties of the tile surface. An inventive step was a realization that the silica sol/cordierite coating applied to the tile surface became boron deficient and increased the silica crystallization or devitrification in the top surface layer. I explain my current invention in part that when boron is introduced into the silica sol/cordierite mixture, the ratio of boron to silica is restored, preventing the surface coating from deteriorating at high temperature. As a result, my invention works at a higher temperature than it did in the prior art.

12. I believe many boron compounds will work in the slurries of my invention. One reason for this is that under high temperature conditions, the boron compounds react to provide oxides, which I suspect are the real active agent. Since the boron compounds turn into the active ingredient upon exposure of high temperatures to the application, I would say most boron compounds would work in the slurries of my invention.

13. In candor, there are a number of boron compounds that are less preferred. I described this in paragraph 18 of my application: "Preferred compounds include those that do not produce an acid that can attack the ceramic insulation". As an example, silicon hexaboride ( $\text{SiB}_6$ ) or silicon tetra boride ( $\text{SiB}_4$ ) is a commonly known emissivity agent. When  $\text{SiB}_6$  is added to the silica sol/cordierite mixture of my previous patents to act as both emissivity agent and a boron source to prevent devitrification, a problem was observed. The  $\text{SiB}_6$  was found to be hygroscopic and under certain conditions had a tendency to absorb moisture and break down into boric acid, which ends up attacking the tile. With this caveat, which as noted is expressed in my application at paragraph 18, I would say those of skill in the art upon reading my application would conclude that all boron compounds could be used in my slurries.

14. For practical reasons, I have not been able to run a control experiment using my prior art slurries with molybdenum silicide on one hand and boron carbide on the other to demonstrate the superior high temperature stability protection potential of the latter formulation. However, based on my knowledge and experience in the field and the discussion above, I would predict that molybdenum silicide would not be effective at raising the temperature stability of a

tile treated with a slurry containing it. In some cases a high emissivity coating (from a high emissivity agent like molybdenum silicide) is not of value say in aircraft applications. In other cases I have found that molybdenum silicide has a detrimental effect. Studies performed has shown when a coatings like TUF1 that contain molybdenum silicide is exposed to lower temperatures around 1000°F for long periods of time the coating deteriorate catastrophically. In an analysis it was found that molybdenum had formed crystals causing a coefficient of expansion mismatch between the tile and the TUF1 coating.

15. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated:

8/13/04

By:

  
Robert A. DiChiara, Jr.